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(54) Title: HIGH MOLECULAR WEIGHT POLYVINYLPYRROLIDONES AND METHOD FOR THEIR PREPARATION (57) Abstract An uncrosslinked, water-soluble polyvinylpyrrolidone having a K-value in excess of 120 and containing less than about 0.1 percent by weight of residual monomer. A method for preparing the high molecular weight polyvinylpyrrolidone is also disclosed. <div style="text-align: right; transform: rotate(-90deg); font-weight: bold; font-size: 1.2em;">Best Available Copy</div>		

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HIGH MOLECULAR WEIGHT POLYVINYLPIRROLIDONES
AND METHOD FOR THEIR PREPARATION

BACKGROUND OF THE INVENTION

I. Field of the Invention

5 The invention relates to a novel high molecular weight water-soluble polyvinylpyrrolidone. In addition, the invention relates to a novel method for the production of water-soluble polyvinylpyrrolidones having a K-value of from about 120 to 150.

II. Background of the Invention

10 Polyvinylpyrrolidone is a well-known polymer having numerous applications in the pharmaceutical, cosmetic, agricultural, food, and other industries. Various methods for its preparation from the monomer N-vinyl-pyrrolidone are known. Normally, the polymeri-
15 zation is carried out either in aqueous solution or in suspension in an organic or non-solvent in the presence of a free radical initiator.

One of the problems with solution polymerization methods for the polymerization of N-vinyl-pyrrolidone is that an upper limit of the molecular weight has become an

- 2 -

obstacle. In particular, the solution polymerization processes known give commercially useful products having K-values of from about 10 to 90. As used herein, the K-value is the so-called Fikentscher K-value which is obtained by
5 capillary viscometry utilizing the relative viscosity of a 0.1% w/v solution in water. (See, U.S. Patent 4,190,718, columns 5 and 6.) This K-value is related to the molecular weight of the polymer in a well-known manner and is conventionally used to characterize the molecular weight of poly-
10 vinylpyrrolidone.

One of the problems with the solution polymerization processes is that the viscosities of dilute aqueous solutions of polyvinylpyrrolidone products having K-values up to 90 are quite low. For example, they normally are in
15 the range of less than 2 mPa.s in 2% aqueous solution.

For various uses, such as, thickeners, cosmetic formulations, printing inks, and the like, higher viscosities are required. For example, other polymers, such as, polyacrylic acids in 1 to 3% solutions, exhibit
20 viscosities of 100 mPa.s.

Numerous attempts have been made to produce higher molecular weight polyvinylpyrrolidone which exhibits higher viscosities in aqueous solution. Generally, these have used the crosslinking of polyvinylpyrrolidone using
25 crosslinking agents. (See, for example, U.S. Patent 4,433,112.) In this method, a starting material of polyvinylpyrrolidone having a K-value of from 30 to 90 is treated by heating an aqueous solution of the polyvinylpyr-

- 3 -

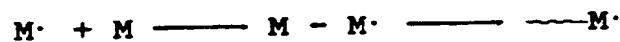
rolidone in the presence of a water-insoluble organic peroxide and the absence of air. Generally, these methods start from an already polymerized polyvinylpyrrolidone.

The polymerization of N-vinylpyrrolidone in the presence of a free radical initiator as well as the mechanism of the polymerization is known. The polymerization consists of a sequence of four steps, namely, (1) initiation; (2) propagation; (3) transfer; and (4) termination. In general terms, these steps may be depicted as follows:

1. Initiation



2. Propagation



3. Transfer

3a. To monomer



3b. To polymer

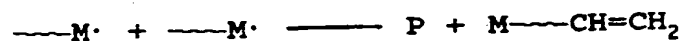


4. Termination

4a. Coupling



4b. Disproportionation



In the foregoing formulas, the symbols have the following meanings:

- 4 -

	R·	a radical from the free radical initiator
	M	monomer
	M·	radical monomer
5	—M·	polymerized monomer radical
	P	polymer
	—M-M—	higher molecular weight polymer
	M—CH=CH ₂	polymer with terminal unsaturation

As the polymerization proceeds and the amount of
10 higher molecular weight polymer concentration in the
reaction mixture increases, and the viscosity also
increases. The increased viscosity has the effect of
hampering the movement of the various moieties at their
various states of polymerization in the mixture. This, in
15 turn, decreases the possibility and the probability of the
individual entities in the mixture from coming together to
form additional polymer whether the entities are in the
radical form or the polymer form. In essence, the various
entities in the reaction mixture increasingly lose their
20 mobility due to the increased viscosity of the mixture.
Also, of course, for any given level of viscosity of the
mixture, the larger molecular weight moieties will always
have less mobility in the mixture than the lower molecular
weight moieties.

25 As a practical matter, this lack of mobility is
adverse to the propagation step but favors termination
making it difficult to obtain a product having a molecular

- 5 -

weight in excess of that represented by a K-value of about 90.

SUMMARY OF THE INVENTION

We have discovered a novel water-soluble poly-
5 vinylpyrrolidone having a K-value in excess of 120 and containing less than about 0.1% by weight of residual monomer without crosslinking. We have further discovered that the high molecular weight polyvinylpyrrolidone of the invention may be prepared by subjecting a solution of N-vinylpyrrolidone monomer in water to polymerization conditions utilizing a free radical initiator and adding water and initiator to the reaction mixture incrementally in amounts and in time periods during the polymerization so that the propagation phase of the polymerization is maximized and the
10 termination phase is minimized by the control of the process parameters. In addition, by adding a chelating agent to the reaction mixture, we have found that it is possible to minimize the residual amount of vinylpyrrolidone monomer in the polymeric product.

20 The product obtained is highly useful since it is not only of a high molecular weight, it exhibits excellent solubility in water. As used herein, high or excellent solubility means a solubility ratio of 5 as in accordance with the description in Preparative Methods of Polymer Chemistry; Sorenson and Campbell, Interscience, 1961;
25 p. 54.

- 6 -

Specifically, we have discovered that control of water and initiator addition allow one to control the individual phases of the polymerization so as to allow increased mobility of the reacting moieties and thus allow the reaction to proceed to higher molecular weight final products than has heretofore been possible. By controlling the addition of water and making the addition of initiator incremental and spacing it over the course of the reaction, it is now possible to increase the propagation phase so as to reach higher molecular weights.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Important control parameters for the inventive process are:

- a) The initial charge of initiator must be accurately controlled and treated. Thus; it is best to maintain the initiator between about 30 to 40°C until it is added to the reactive mixture. Also, the amount should be accurately measured to be within the ranges specified herein.
- b) The temperature should be controlled within the specified range herein throughout the reaction. While the reaction is exothermic, it proceeds relatively slowly; thus moderate cooling is required during the reaction.
- c) It is important to control the viscosity of the reaction mixture, particularly during the

- 7 -

reaction period from 4 to 7 hours after initiation of the reaction. This is achieved by adding water incrementally to maintain the viscosity constant during this period. The constant viscosity at this stage of the reaction permits growth (propagation) of the molecular chains.

- d) Atmospheric environment must be kept inert, i.e., with a nitrogen or inert gas purge.

These parameters are discussed in detail herein-

below.

The initial reagents need not be purified, although reactions have been carried out with N-vinylpyrrolidone which has been treated with activated carbon. While the reaction rate is somewhat faster than those with non-treated monomer, it is imperative that the monomer be filtered to remove all traces of carbon, which otherwise, can stop the reaction before high conversions are reached.

The initial concentration of monomer can have a significant effect on obtaining the inventive product. The initial monomer concentration should be kept in the range from about 25 to 40% by weight based on the total weight of water and monomer. If the initial monomer concentration is below about 25% by weight, the inventive product is not obtained in any useful yield. When the initial monomer concentration is greater than about 40%, increased agitation is required to achieve uniformity of the reaction mixture because of the relatively high viscosity. The greater agitation results in increased shear which produces

- 8 -

an undesirable shift in favor of the termination phase and adverse to the propagation phase. Most preferably, we have found that a monomer concentration of 27 to 28% by weight is most desirable.

5 Of particular importance with the present invention is utilizing an incremental addition of the initiator, i.e., adding the initiator to the reaction mixture more than one time. This has the effect of maintaining the reaction mixture viscosity uniform. It also increases the
10 initiator efficiency resulting in an increase in the molecular weight of the vinyl product and a decrease in the amount of residual monomer. Specifically, we have found that the total amount of initiator added should be in at least two separate additions, the first, initially to begin
15 the reaction, and the second at a later point in the reaction. It is also possible to add the initiator in three or four or more increments. We have found that two or three increments is preferred.

 The total amount of initiator added generally is
20 in the range from about 0.01 to 2.0% by weight based on the monomer and preferably, from about 0.1 to 0.2. The amount added at each incremental addition would be an appropriate half, third, or the like of the total amount to be added.

 The timing of the addition of the initiator may
25 be varied over the course of the total time period of the reaction. Thus, if three additions are used (including the initial addition of initiator), the second and third additions could be spaced at one-third intervals over the

- 9 -

entire course of the reaction. Similarly, the addition of initiator when only two additions are made could be at the half-time of the reaction. However, we have found in a preferred embodiment that when two additions of initiator
5 are utilized (one in addition to the initial addition of initiator), the second is made at approximately the three-quarter point in the reaction.

We have also found that the addition of a buffering and chelating agent is critical in obtaining a
10 product with low residual monomer. This agent performs a dual function in the reaction. Specifically, it complexes with traces of heavy metals introduced by the aqueous medium or by the reactor, which metals normally contaminate the product and poison the catalytic initiator. The
15 buffering agent also controls the pH at a critical level of not less than 5.5, preferably to a level on the basic side between about 6.1 and about 10. Below a pH of 5.5 the vinylpyrrolidone rate of polymerization is too slow to compete with the more active quaternized comonomer. thus,
20 when the level approaches 5.5, additional quantities of buffer are added to increase basicity. Generally, the amount of buffer employed represents between about 0.01 to 0.5 weight %, preferably between about 0.04 to 0.3 weight % of the vinylpyrrolidone monomer. Suitable agents which
25 combine buffering and chelating activity are those which have a pH greater than 5 and include ethylene diamine tetraacid disodium salt, tetrasodium pyrophosphate, anhydrous dibasic sodium phosphate + monobasic potassium

- 10 -

phosphate, borax, sodium carbonate + sodium bicarbonate, tribasic sodium phosphate and calcium hydroxide. These buffering agents are employed as 0.005 molar to saturated aqueous solutions at 25°C. If the amount of buffer is too great, the ash content of the product may increase beyond product specification. For example, for pharmaceutical end uses, the ash should be less than about 0.1% by weight. However, for non-pharmaceutical uses, higher ash contents can be tolerated, e.g., up to about 0.5% by weight.

10 However, if the amount of buffer is too low, the residual monomer content will be intolerable.

During the course of the polymerization, the viscosity of the reaction system increases. The viscosity can be measured in a variety of manners, e.g., torque measurements and the like. Typical of such devices are the Heller HST-10 stir tester. We have discovered that by initiating the addition of water to the reaction mixture at a point in the reaction after a given amount of conversion to polymer has been achieved, and by adding this water in a controlled manner, the viscosity of the reaction mixture can be maintained within a desired range of values so as to the propagation phase of the reaction and minimize the termination phase. This results in achieving the desired higher molecular weight product. Normally, the water is added over a period of time at a constant feed rate with appropriate stirring to maintain the viscosity constant. While the addition of water may be started at various times during the reaction and continued for various periods of

- 11 -

time during the reaction, we have found that it is best to add the water after a monomer conversion of from about 75 to 90% and preferably, from about 80 to 82%. This corresponds to a reaction time of from about 210 to 240 minutes after the initiation of the reaction, when the reaction is carried out at approximately 57-58°C. Depending on the other parameters under which the reaction is carried out, the time of addition of the water and the period of addition over which the water is added can be varied. What is important, however, is the discovery that by the addition of water in this manner as well as the variation of the other significant parameters as discussed hereinabove, the propagation phase of the reaction can be prolonged leading to higher molecular weight products.

Normally, the polymerization reaction is carried out under an inert atmosphere. We have found that a nitrogen purge is most desirable, although other inert gases can be used.

The temperature at which the reaction is carried out does have an effect on the ultimate K-value of the polymer. Also, understandably, the temperature has an effect on the total time needed to carry out the reaction. Lower temperatures would require a more prolonged reaction time, whereas higher temperatures would lead to a shorter and perhaps uncontrollable polymerization as well as possible degradation of ingredients and/or product. We have discovered that the preferred temperature range for

- 12 -

the reaction is from about 55 to 65°C and most preferably, from about 57 to 60°C.

An important aspect of the invention is the conversion of the product into a dry powder. Thus, for many applications, the product must be redissolved in water and generally, dissolution rate decreases with decreasing particle size. Normally, this would be achieved by removing the water from the reaction mixture and pulverizing the product. However, care must be taken in these final steps to avoid degradation of the product (resulting in a decreased molecular weight). In particular, we have found that the most desirable procedure is to utilize a drum dryer to produce the polymer in sheet form. Alternatively, a belt dryer may be used. The sheet is immediately passed through a pin shredder to break it into flakes and flakes are then ground to a desired powder size. Particularly important in this procedure is that the product solution be dried as soon as possible after the reaction is complete to avoid any detrimental change in the product.

In particular, using either drum or belt drying, a product having a water content below about 4.5 weight percent without any K-value degradation is obtained the drying temperature is generally in the range from about 250 to 260°C for belt drying and about 290 to 330°C for drum drying.

The dried product is then ground in a manner to minimize K-value degradation. While a variety of grinding

- 13 -

devices may be used, we have found a Fitzmill to be particularly satisfactory. In particular, acceptable powder was produced using a Fitzmill with a 0.094 inch screen and rotor speed of 3600 rpm. the desirable product is in the form of a powder of which 80% is between 16 and 40 mesh and less than 10% passes a 40 mesh screen (U.S. Standard).

The following example illustrates the present invention:

For this reaction, a 12 liter reactor equipped with a condenser, an anchor agitator with a speed/torque readout, a thermocouple, a nitrogen inlet, and a dropping funnel were utilized. All of the reagents were used without purification. Nitrogen was bubbled through the reaction mixture during the entire course of the reaction.

4,541 grams of deionized water and 1.69 grams of tetrasodium pyrophosphate were added to the reactor and mixed at 110 rpm for 5 minutes. The agitation was stopped and then 1,687 grams of vinylpyrrolidone were added after it was assured that the tetrasodium phosphate had been completely diluted. The agitator was again turned on and maintained at approximately 110 rpm. A nitrogen purge was initiated through the reaction mixture. The reaction mixture was heated to and held at a temperature of 53-54°C and then 1.67 grams of t-butylperoxypivalate was added. This time was taken as time zero. Any residual initiator clinging to the sides was washed from the interior of the reactor with a small amount of water. The reaction exotherm brought the temperature into the range of from

- 14 -

about 57 to 60°C. This temperature range was maintained during the next 420 minutes of the reaction. Neither heating nor cooling was required to maintain the temperature. (If needed, heat may be supplied at approximately
5 57.5°C and terminated at 58.5°C to maintain the reaction temperature uniform.)

After 210 minutes, the addition of deionized water was begun at a feed rate of 10.4 grams per minute. The total amount of water added in this manner was 2,187
10 grams so that the feed was completed after a reaction time of 420 minutes (a total feed time of 210 minutes). The water was added continuously using a dropping funnel. The addition rate of water was monitored by measuring the torque of the polymerization mixture. In this example, the
15 agitator was set at 110 rpm and the torque was maintained to at least the value observed at 210 minutes.

At this point, the conversion of monomer was about 80 to 82%. The reaction mixture had a Brookfield viscosity of 40,000 cps at 57°C, and the K-value of the
20 polymer was 105 ± 2 . The torque was 14.5 oz-inch.

At 330 minutes, a second addition of t-butylperoxypivalate (1.77 grams) was effected and any residual initiator washed from the inside of the flask with a small amount of water. At this point, the conversion was between
25 85 and 87%. This second amount of initiator was added at a time when the concentration of monomer and polymer was 23% by weight.

- 15 -

At 420 minutes, the polymerization was terminated by heating the reaction mixture to $80 \pm 2^\circ\text{C}$ within a period of 15 minutes and holding it at this temperature for an additional 15 minutes to thus polymerize remaining monomer.

5 At this point, the conversion of the monomer was 98 to 99.5%, and the concentration of polymer/monomer about 20%. At 450 minutes, the reaction was terminated by turning off the nitrogen purge and cooling the reactor. The reactor was discharged at $55-60^\circ\text{C}$, the residual monomer of the
10 polymer product in aqueous solution was less than 0.2% which is the limit of detection and the K-value of the polymer was 119-125.

A series of polymerizations were carried out in glass wherein the amount of chelating and buffering used
15 (tetrasodium phosphate) was varied with the remaining reaction parameters being the same as described above. The results are depicted in the Table. As shown therein, while it is possible to achieve K-values greater than 120 even in the absence of the chelating agent, the percent of residual
20 vinylpyrrolidone monomer is extremely high (0.23%). In contrast, with even a relatively small amount of the TSPP, (0.01 weight %), the residual monomer is minimized.

For the results tabulated in the Table, the residue on ignition and residual vinylpyrrolidone monomer
25 were determined as follows:

Residue on Ignition

10 g of sample were weighed in a crucible that had previously been ignited, cooled, and weighed. The

- 16 -

crucible was heated gently at first until the sample was thoroughly charred. It was then cooled and the residue moistened with 2.0 ml (1:1) of sulfuric acid and heated gently until white fumes no longer evolved. The sample was then ignited at $800^{\circ}\text{C} \pm 25^{\circ}\text{C}$ until the carbon was consumed. It was cooled in a desiccator, weighed and the ash content was calculated as follows:

$$\% \text{ ash} = \frac{W_2 - W_0}{W_1 - W_0} \times 100$$

wherein W_0 = crucible weight
 W_1 = sample and crucible before ashing
 W_2 = sample and crucible after ashing

Determination of Percent Vinylpyrrolidone

A sample was weighed into a 250 ml Erlenmeyer flask, the sample was dissolved in 10 - 20 ml of distilled water or reagent grade alcohol as required. 10 ml of 5% sodium acetate is added. If the solution is cloudy, reagent alcohol is added until the solution clears. The contents are mixed well and then titrated with a 0.1 N iodine solution until a straw color appears. An additional 5 ml of the iodine solution is added. The total amount of iodine added is recorded.

The flask is swirled and set aside for 5 minutes. If the color disappears at the end of this time, 3 additional ml of iodine are added and the contents are allowed to stand for 3 minutes. The amount of iodine of additional iodine solution added is recorded.

- 17 -

The solution is then titrated with 0.1 normal sodium thiosulfate until it is a light yellow. 5 ml of starch indicator is added. If alcohol is used as a solvent, the solution should be titrated without the starch because starch gives a poor endpoint. The titration is continued until a sharp colorless endpoint is obtained.

The percent vinylpyrrolidone is then calculated using the following formulas

10 1. % VP =
$$\frac{[(ml_i \times N_i) - (ml_{thio} \times N_{thio})] 5.555}{g \text{ sample}}$$

2. % VP =
$$\frac{[(ml_i \times N_i) - (ml_{thio} \times N_{thio})] 555.5}{g \text{ sample} \times \% \text{ solids}}$$

-18-

TABLE 1

<u>Run No.</u>	<u>Wt. % TSPP</u> <u>On Wt. VP</u>	<u>% Solids</u>	<u>Residue on</u> <u>Ignition</u> <u>(On 100%</u> <u>Solids)</u>	<u>K-Value</u> <u>0.1% Water</u>	<u>10%</u> <u>Soln</u> <u>% VP</u>	<u>pH</u> <u>As Is</u>	<u>pH</u> <u>5% Soln</u>
1	0.10	10.4	0.13	138	0.04	7.60	6.68
2	0.05	10.4	0.05	137	0.06	6.85	6.42
3	0.01	10.3	<0.03	137	0.05	6.75	6.38
4	0.00	10.9	<0.01	122	0.23	6.20	5.61

- 19 -

WHAT IS CLAIMED IS:

1. Polyvinylpyrrolidone which is water-soluble and non-crosslinked, has a K-value in the range from about 120 to 150, and a residual monomer content of less than about 0.1 percent by weight.

2. The polyvinylpyrrolidone of claim 1 in the form of a dry powder.

3. The polyvinylpyrrolidone of claim 2 wherein about 80% of the powder is between about 16 and 40 mesh and less than about 10% is less than 40 mesh.

4. The polyvinylpyrrolidone of claim 3 having a water content of less than about 4.5%.

5. A method for producing the polyvinylpyrrolidone of claim 1 comprising the steps of:

- a) forming a mixture of N-vinylpyrrolidone monomer, a chelating buffer, and water;
- b) subjecting the reaction mixture to polymerization conditions in the presence of an initiator for a period of time to convert substantially all of the monomer to polyvinylpyrrolidone;

- 20 -

- c) during the polymerization, maintaining the viscosity of the reaction mixture sufficiently constant so as to maximize the propagation phase and minimize the termination phase of the polymerization.

6. The method of claim 5 wherein the initial reaction mixture contains from about 25 to 40 percent by weight monomer based on the weight of water and from about 0.05 to 0.5 weight % of chelating buffer.

7. The method of claim 5 wherein the polymerization is carried out at a temperature in the range from about 55 to 65°C.

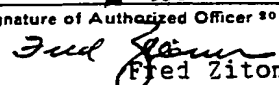
8. The method of claim 1 wherein the viscosity is kept constant by the incremental addition of water and initiator to the reaction mixture.

9. The method of claim 5 wherein after termination of the reaction, the product is dried in a belt or drum dryer and the dried product is ground to a powder of which about 80% is between 16 and 40 mesh and less than about 10% is less than 40 mesh.

10. The method of claim 9 wherein the product is dried to a water content of less than about 4.5%.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US91/02115

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): C08F 26/08, 26/10, 22/38; A61K 31/79 U.S. CL: 526/264, 263, 258; 525/326.7, 326.8; 424/80		
II. FIELDS SEARCHED		
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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category [*]	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X Y	US, A, 3,862,915 (FRIED) 28 JANUARY 1975; See entire document.	1, 5-8 2-4, 9, 10
Y	US, A, 4,058,655 (DENZINGER) 15 NOVEMBER 1977; See Column 4, lines 4-30.	2-4, 9, 10
Y	US, A, 4,190,718 (LORENZ) 26 FEBRUARY 1980; See Column 2, line 47 and Column 7, line 36.	2-4, 9, 10
A	US, A, 4,554,311 (BARABAS) 19 NOVEMBER 1985; See entire document.	1-10
A	US, A, 4,433,112 (STRAUB) 21 FEBRUARY 1984; See entire document.	1-10
A	US, A, 4,053,696 (HERRLE) 11 OCTOBER 1977; See entire document.	1-10
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹ 02 MAY 1991	Date of Mailing of this International Search Report ² <div style="font-size: 1.5em; font-weight: bold; text-align: center;">05 JUN 1991</div>	
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